THIRD QUARTERLY REPORT

DEVELOPMENT OF CADMIUM SULFIDE

THIN FILM PHOTOVOLTAIC CELLS

BY

F. A. SHIRLAND, J. R. HIETANEN, F. AUGUSTINE, and W. K. BOWER

PREPARED FOR

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

CONTRACT NAS 3-6461

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ELECTRONIC RESEARCH DIVISION

CLEVITE CORPORATION

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INTRODUCTION AND SUMMARY

Increased funding enabled the scale of effort to be appreciably increased in this period. This provided support for the frontwall metal substrate cell laboratory pilot line, for intensive stability studies, and for design and performance improvements. As a result, major strides have been made in the development of the thin film CdS solar cell.

The output of the plastic substrate cell has been brought up to the level of the metal substrate cell. Both metal and plastic substrate large area (50 cm^2) cells have averaged 5% conversion efficiency in this quarter.

Many of the metal substrate and the plastic substrate cells have been stable for extended periods after an initial adjustment in output during the first few days. Studies to date have disclosed no inherent instabilities for the CdS thin film solar cell. Rather, all indications are that most instabilities experienced in the past can be attributed to either moisture absorption or to a loosening of the collector grid.

At the end of this period it became apparent that the present Clevite barrier formation process produces large area cells with latent efficiencies of about 7%, but that hitherto incomplete collection of the current by the collector grid has prevented its realization. Changes in the conditions of cell lamination produced a number of large area cells with initial efficiencies in excess of 7%. The highest output obtained was 7.8% for a 50 cm^2 area cell with a short circuit current density of 24 mA/cm^2 and a fill factor of 70%.

The highest output obtained from a plastic substrate large area cell was 7.1% with 22 mA/cm^2 short circuit current, 67% fill factor, and a power to weight ratio of 88 watts per pound. Design changes presently in process indicate that power-to-weight ratios well in excess of 100 watts-per-pound should be realized in the next period.

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CdS FILM EVAPORATION

Double Layer Films

The idea of the double layer film for thin film solar cells is to have the bulk of the semiconductive film highly conducting to minimize series resistance effects and to have the thin surface layer on which the barrier is formed poorly conducting so that a better junction can be obtained. Earlier reports[1] described studies of indium doped, undoped, and copper counter-doped CdS films and the characterization of such films for use in double layer cells. While these studies were not complete, the results led to the use of indium doped CdS films of 0.01 ohm-cm resistivity for the lower (highly conducting) layer, and of undoped CdS of 10 to 100 ohm-cm for the upper layer.

In this period a number of double layer films were evaporated along these lines and processed into cells. Table I lists the data on some of these and the outputs of the resultant cells. The best cell efficiency obtained was 5.5% for a 3" x 3" size cell. While this is comparable with standard single layer film cells processed at the same time, it was short of what was hoped for.

However, the tooling for these evaporations was not adequate to carry out two successive evaporations (without breaking vacuum) of differently doped charges at the same rates normally employed for single evaporations. Further, other processing difficulties such as lamination variations tended to mask the effects of the double layer films. Hence, it is felt that the results obtained were not truly indicative of what might be obtained with the double layer film technique.

In view of these complications and the press of other higher priority problem areas, further work on the double layer films has been postponed.

Very Thin Films

Additional experiments on very thin CdS film evaporation were carried out using the hot wall closed chamber technique and tooling described in the last report. It was found that the difficulties encountered earlier with the CdS film re-evaporating from the 600°C substrate could be prevented by

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TABLE I

DOUBLE LAYER CdS FILM CELLS ON MOLYBDENUM SUBSTRATES

Cell No.	Layer	Thickness	Material	OCV (v)	J (mA/cm^2)	Fill (%)	Eff. (%)
A557	Lower	1.0 mils	Indium Doped ~ 0.01 ohm-cm	0.482	14.8	51	3.6
	Upper	0.2 mils	Undoped ~ 10-100 ohm-cm				
A572	Lower	1.0 mils	Indium Doped ~ 0.01 ohm-cm	0.418	17.1	58	4.2
	Upper	0.2 mils	Undoped ~ 10-100 ohm-cm				
A578	Lower	0.95 mils	Indium Doped ~ 0.01 ohm-cm	0.469	15.2	59	4.3
	Upper	0.35 mils	Undoped ~ 10-100 ohm-cm				
A580	Lower	0.50 mils	Indium Doped ~ 0.01 ohm-cm	0.450	18.1	68	5.5
	Upper	0.40 mils	Undoped ~ 10-100 ohm-cm				

Notes: All cells 50 cm^2 area

No overlap of evaporation of two layers

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lowering the hot wall temperature to about 550°C. Also, it was found that much smaller charges were required as a much higher proportion of the CdS that was evaporated condensed on the substrate. Further, at these relatively high substrate temperatures, the CdS had to be pre-doped to secure reasonable film conductivities. Approximately 0.05 to 0.067 mol% indium in the charge gave film resistivities of 10 to 100 ohm-cm.

Films were evaporated under these conditions on 0.002" thick molybdenum substrates. They appeared to be uniform in thickness and texture and free from pin holes, spatter or other flaws. They had excellent adhesion and had no tendency to curl. Figure 1 shows the structure of one such film as disclosed by the electron microscope. The grains are smooth surfaced, well delineated and up to 5-10 microns across, or about the same order as the film thickness. The structure of these is comparable to that found by workers at Harshaw[2] on thicker films formed at 600°C, except that the grains are smaller.

A total of 48 such "very thin" films were evaporated on molybdenum substrates at 600°C in this period, and a number of these were processed into small area (1 x 2 cm) cells as shown in Table II. All of the films thinner than 4.5 microns shorted when barriers were processed on them, even though no pre-etch and very short dip times were employed. Films in the range of 4.5 to 6.5 microns thickness gave cells with efficiencies up to 3.3%. These cells had good open circuit voltages and reasonable characteristic curves. They were low because of low currents. It is believed that this was a result of incomplete "activation" because of the short barrier dip times.

It seems probable that high efficiency large area CdS film cells can be made from films of less than 5 microns thickness, but a considerably expanded effort might be needed to acquire the necessary technology. Films of 5 to 10 micron thickness, formed at intermediate substrate temperatures of 300 to 400°C seem more likely to produce acceptable cells within the limitations of the available effort. Hence, the work will be directed along these lines in the final quarter.

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9800X

FIGURE 1. STRUCTURE OF CdS FILM EVAPORATED AT 600°C SUBSTRATE TEMPERATURE

Film C-74 Etched 8 sec. in 1:3 HCl Solution - Palladium Shadowed Carbon Replica.

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TABLE II

CELLS FABRICATED FROM CdS FILMS EVAPORATED AT 600°C SUBSTRATE TEMPERATURE

Cell No.	Indium Doping (Mol%)	Film Thickness (μ)	Barrier Dip Time (sec)	CELL OUTPUT OCV (v)	J (mA/cm^2)	Fill (%)	Eff. (%)	Remarks
C36	none	15.2	5	0.35	10.8	--	1.5	High R$_s$
C43	0.5	1.3	5	--	--	--	--	Shorted
C56	0.5	2.5	2	--	--	--	--	Shorted
C57	0.5	2.8	0.5	--	--	--	--	Shorted
C64	none	2.8	5	--	--	--	--	Shorted
C65B	0.05	5.1	5	0.50	10.2	65	3.3	
C65C	0.05	5.1	1	0.50	11.7	65	3.3	
C66	0.066	2.8	1	--	--	--	--	Shorted
C67F	0.066	6.3	1	0.465	12.6	57	3.3	
C67G	0.066	6.3	1	0.455	10.8	61	3.1	
C67H	0.066	6.3	1	0.465	10.8	62	3.1	
C70E	0.05	4.5	1	0.47	12.0	44	2.4	High R$_s$
C71	0.05	2.8	1	--	--	--	--	Shorted
C75-1	0.05	12.7	1	0.46	9.6	45	1.9	High R$_s$
C75-2	0.05	12.7	1	--	--	--	--	Shorted

Notes: All cells evaporated with substrate at 600°C and Hot Wall at 550°C.
All cells 1.67 cm^2 area, on 0.002″ molybdenum substrates.
Cell C-56 had 1 sec. HCl pre-etch -- others had no pre-etch.
Some of the series resistance effects may have been due to incomplete lamination.

Moderately Thin Films

The first attempt to use moderately thin CdS films for solar cells was with an 11.4 micron thick film evaporated at 350°C on an 0.002" thick molybdenum foil substrate. The Veeco evaporator with standard tooling was used. The substrate was 3" x 3" in size set at 5-1/2" from the evaporation sources. This was not a closed chamber hot wall type of evaporation.

The film looked very good, and was cut into smaller pieces and processed into cells as summarized in Table III. Cell efficiencies of 4.5, 5.0, and 5.3% were obtained when dip times comparable to standard practice were used. It is to be noted that as the barrier dip time was increased the OCV fell somewhat but the current output increased. These results are very encouraging and more cells of this type will be made in the final quarter.

Orientation Effects

Early in this report period a slump in the output of the standard process molybdenum substrate cells from the previous 5% level to a 3.5% level was experienced. This slump coincided with a factoring up of the scale of CdS film evaporation in the NRC evaporator from doing four 3" x 3" films at a time to nine at a time. Standard process plastic substrate cells being evaporated in the Veeco evaporator did not show the slump in output.

Subsequent data failed to corroborate the indication that the change in the evaporation process was responsible for the slump, but at the time there was a strong implication that way and hence the NRC evaporation process was examined more closely. In addition to some wide variations in substrate temperatures that were found and immediately corrected, there were marked differences in the appearance of the evaporated CdS films. The middle portion of the 9" square substrate area gave CdS films that were a bright shiny amber in color -- optically clear so that the rear surface of the film could be readily observed with slight magnification. However, the peripheral portion of the 9" square substrate area was duller in appearance, somewhat matte, and not as clear optically.

The tooling for this evaporator consisted of 4 cylindrical evaporation sources set 5-1/2" below the substrate and spaced in a square pattern 4-1/2" on a side symmetrically with relation to the substrate. From this geometry

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TABLE III

CELLS FABRICATED FROM CdS FILMS EVAPORATED AT 350°C SUBSTRATE TEMPERATURE

| Cell No. | Film Thickness (μ) | Barrier Dip Time (sec) | CELL OUTPUT | | | | Remarks |
			OCV (v)	J (mA/cm^2)	Fill (%)	Eff. (%)	
A599-1	11.4	1	0.50	8.5	64	3.6	
A599-2	11.4	1	0.52	8.9	57	3.4	
A599-3a	11.4	2	0.49	13.7	37	3.5	
A599-3b	11.4	3.5	0.48	16.2	57	4.5	
A599-3c	11.4	3.5	0.47	16.5	67	5.3	Good lamination
A599-3d	11.4	5	0.46	17.4	67	5.0	Good lamination

Notes:

CdS Films undoped

Cells A599-1 and 2 were 16.0 cm^2 area.

Cells A599-3a, b, c, and d were 1.67 cm^2 area.

Films evaporated on 0.002" molybdenum substrates.

the center portion of the substrate was essentially normal to the vapors emanating from the sources, while the peripheral area was essentially oblique with a net angle of incidence approaching 45°.

Goldstein and Pensak[3] observed anomolous effects when CdTe films were evaporated at an oblique angle, and these effects were ascribed to differences in orientation of the grains of the polycrystalline film. Looking for such differences in these CdS films, a portion of one 3" x 3" film that was shiny at one edge and dull at the other was examined with the electron microscope.

The films were etched for 8 seconds in HCl (1:3 solution) and palladium shadowed carbon replicas were made and examined. Figure 2 shows the structure of the shiny portion of the film and Figure 3 shows the dull portion. There is indeed a marked difference between the two portions. The shiny part of the film shows the pattern that has generally been attributed to "c" orientation,[4, 5, 6] while the dull portion shows that of off-"c" towards "a" orientation.

The visual differences in grain orientation were eliminated finally by moving the evaporation sources further apart (to 7-1/2" spacing) and increasing the source to substrate distance (to 9"). Before this was accomplished, however, it was noticed that some films with the dull appearance seemed to be giving cells with appreciably higher initial current and power outputs than the shiny films. (It also appeared that these cells might be less stable.) Table IV gives the output data for the standard process large area cells fabricated at the time from films that could be difinitely ascribed as having a "dull" or a "shiny" appearance. Though there were only a few cells involved, there did indeed seem to be a difference in output in the direction indicated. Subsequently there were contrary indications, and it now appears that the effects of orientation such as discussed above are more than masked by other variables in the cell fabrication process.

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FIGURE 2.   STRUCTURE OF CdS FILM EVAPORATED WITH NEARLY NORMAL ANGLE OF
INCIDENCE - SHINY APPEARANCE   (Substrate Temperature 220°C)

10,200X

Film D20B - Portion at Inner Edge of 3" x 3" Film - Etched 8 sec. in 1:3 HCl Solution -
Palladium Shadowed Carbon Replica.

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FIGURE 3. STRUCTURE OF CdS FILM EVAPORATED WITH OBLIQUE ANGLE OF
INCIDENCE - DULL APPEARANCE (Substrate Temperature 220°C)

Film D20B - Portion at Outer Edge of 3" x 3" Film - Etched 8 sec. in 1:3 HCl Solution -
Palladium Shadowed Carbon Replica.

10,200X

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TABLE IV

EFFECT OF EVAPORATION ANGLE OF INCIDENCE ON CELL OUTPUT

"A" Cells - Dull Appearance -- Oblique Angle of Incidence

No.	OCV	J	Fill	Eff %
D19A	0.47	16.3	69.0	5.3
D24A	0.465	19.3	63.5	5.6
D25A	0.47	17.0	67.5	5.4
D27A	0.47	19.7	68.0	5.8
Avg.		18.1	67.0	5.53

"E" Cells - Shiny Appearance -- Normal Angle of Incidence

No.	OCV	J	Fill	Eff %
D19E	0.47	14.5	71.0	4.8
D24E	0.46	15.3	61.0	4.3
D25E	0.47	14.2	69.0	4.6
D27E	0.465	17.0	61.5	4.8
Avg.		15.3	65.6	4.63

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CELL IMPROVEMENT STUDIES

Alternate Metal Substrates

The present frontwall metal substrate CdS thin film solar cell is made with an 0.002" thick annealed molybdenum foil as the conducting substrate. It was selected originally because its thermal expansion coefficient matched that of CdS fairly closely. In practice it was found that molybdenum could be cleaned easily and that CdS adhered very well to it and gave a resonably low resistance ohmic contact. Thus, the frontwall CdS film solar cell was developed using molybdenum foil substrates almost exclusively.

Molybdenum has some disadvantages though, including high cost, high density, poor electrical conductivity. Also it is difficult to attach leads to it by soldering or welding when interconnecting cells into arrays. Lately it has been found very difficult to use thinner molybdenum foils for lighter weight cells even though thinner CdS films should presumably make their use practical. Molybdenum substrates can be chemically milled to about 0.0004" (10 microns) after evaporation of the CdS and cell formation, but this is a laborious and wasteful operation poorly suited to later mass production. Apparently, rolling molybdenum foil down to 0.0005" or even to 0.001" does something to the structure of the metal that prevents well structured adherent CdS films from being evaporated onto them.

Other laboratories have attempted to use alternate metal foils as substrates for CdS film cells, and some preliminary success has been obtained[7] with silver, gold, and Invar foils. However, the technology of using these metals as CdS film cell substrates was not developed to the point where any one of them could satisfactorily replace molybdenum.

Clevite's success with Kapton plastic substrates for CdS thin film solar cells has made it evident that wide differences in thermal expansion coefficients do not necessarily prevent good CdS film adhesion -- even for films approaching 20 microns in thickness. Therefore, some alternate metals are being investigated as substrates for CdS film cells by this laboratory.

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a. <u>Silver</u>

Although silver is slightly heavier than molybdenum it is less expensive and has much better electrical conductivity. It can be secured readily in very thin foils, and can be easily cleaned and etched. A 1.2 mil thick sheet of 99.9% pure silver foil was cleaned and etched and electroplated with zinc to provide a better ohmic contact to CdS. The film was held in the stainless steel "picture frame" holder used for evaporating plastic substrate films and a 0.001" thick film of CdS was evaporated onto a 3" x 3" size sheet. Adhesion was very good and the CdS film appeared to be excellent. Normal evaporation conditions were used.

This film was fabricated without difficulty into a 50 cm^2 area cell which gave an output of 5.3% efficiency. It's OCV was 0.49 volts, the SCC was 860 mA (or 17.4 mA/cm^2), and the fill factor was 65%. These results are comparable to the molybdenum substrate cells fabricated at the same time. After 2 weeks the cell efficiency was 5.1%. Further work with silver substrates is planned.

b. <u>Copper</u>

Copper is 30% less dense than molybdenum, is very inexpensive, and an excellent conductor. It can be obtained in thin foils of varying hardness.

One CdS film cell has been fabricated on copper so far. Electrolytic copper foil was etched chemically to 0.001" thickness, coated by vacuum evaporation with 500 Å of zinc, and then 0.001" of CdS was vacuum evaporated with the regular conditions. The CdS adhered well and processed without difficulty into a 4.4% cell of 50 cm^2 area. It's current density was 12.9 mA/cm^2 and the fill factor was 65%. This material also looks very promising.

c. <u>Aluminum</u>

Several attempts have been made to deposit CdS films on aluminum foil substrates of 0.001" thickness, but so far without success. This is somewhat puzzling as there have been occasions when CdS films have adhered very well to aluminum fixtures used in the vacuum chamber. Some

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additional work will be done with this material since its lightness and availability would make it very advantageous.

d. Zinc

Several sheets of zinc foil were obtained for trial as CdS film cell substrates. On etching it was observed that this material had a very large grain structure clearly visible without magnification. The chances of obtaining good structured CdS films on such material are believed to be very low. A check of the metallurgy of zinc makes it seem unlikely that zinc foil can be obtained without a high degree of recrystallization. Hence, none of this material was actually tried and no further work with it is planned at present.

Thinner Molybdenum Substrates

Attempts have been made to reduce the thickness of the molybdenum foil substrate in order to reduce the weight of the cell and thus increase the power to weight ratio. A method was developed at another laboratory[8] of starting with 0. 002" thick molybdenum, leaving the back of the cell open when laminating, and then chemically milling the molybdenum to about 0. 0004". This does appreciably reduce the cell weight. This technique has been tried in this laboratory also, and Kapton encapsulated large area cells were fabricated which consistently gave power to weight ratios of 50 watts per pound.

This is a painstaking way of achieving thinner cells and much less desirable than starting with thinner material in the first place. Earlier attempts to use thinner molybdenum foils were not very encouraging as they were difficult to handle (due to a tendency to kink and get dented) and there were severe curling problems.

Clevite's experience and recent success in handling Kapton plastic for CdS cell substrates made us hopeful that similar handling of thinner molybdenum foils might be effective in getting around these difficulties. Hence, several runs were attempted using 0. 0005" and 0. 001" molybdenum foil obtained from the General Electric Company. The same substrate holders and other tooling and handling procedures normally used for the

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plastic substrate cells were used for these runs.

These methods were indeed successful in getting around the earlier handling difficulties. However, difficulties were encountered with poor CdS film adhesion. Most of the films spalled so badly that cells could not be fabricated from them. In one instance fair adhesion was obtained with only minor spalling around the edges for a film on an 0.0005" thick substrate. The efficiency of the cell fabricated from it was only 3.7% with a very poor fill factor -- probably because of high series resistance.

In view of more promising indications from the thinner copper and silver substrates, further work on the thinner molybdenum foil substrates has been indefinitely postponed.

Collector Grids

a. Cleaning

The vendor of the electroformed metal mesh grids has no special provisions for cleaning the grids. After electroforming, the grids are water rinsed, dried, inspected, packed between sheets of acetate film and shipped. In view of the known sensitivity of CdS cell barriers to certain types of contaminants it is desirable to remove all doubts regarding the possibility of such contamination from the grids and establish a procedure to clean the grids prior to use.

Several possible methods of cleaning the copper grids were therefore evaluated. Included were soaks in sulfuric acid solution, in sulfuric acid-sodium dichromate solution, in hydrochloric acid solution, and in trichlorethylene solvent. Cells were fabricated using grids cleaned by soaking in each of the above solutions, and also using grids that had been cleaned in each solution 2, 7, 14, and 35 days earlier.

While the data were insufficient to draw a positive conclusion, best results seem to have resulted with grids cleaned in the HCl solution, and not stored for more than 7 days prior to use. The cleaning process consists of a 10 second soak in 1:10 HCl (AR grade) solution at room temperature, followed by 3 separate distilled water rinses, an acetone rinse and final drying in an argon stream. This process has been adopted for cleaning all electroformed copper grids used in our cells.

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b. Cemented Grids

Earlier, a technique was developed and reported[9] for cementing the collector grids in place using a conductive silver epoxy composition. Nine 3" x 3" frontwall cells were fabricated with such cemented collector grids which had efficiencies between 3.6 and 4.9%. These were delivered to Lewis Research Center of NASA for evaluation.

NASA placed these cells on their standard vacuum thermal cycling test to determine if this method of CdS cell contacting would be successful in preventing the cell shorting that had been experienced on some frontwall metal substrate cells with the collector grid held in pressure contact by the plastic encapsulation.

No shorts were observed on any of these cells. However, a slow steady degradation in output was observed, and after about 1500 cycles the cells had dropped to about 10% of their initial output.

It was thought that the degradation must have been caused by some deleterious substance in the conductive epoxy cement used. These cements are not normally of semiconductor grade purity, and it takes only traces of some impurities to poison the output of CdS cells in just the fashion observed for these cells. Hence, some attention has been given to this aspect and a number of different commercial conductive epoxy cements were obtained for analysis and evaluation. So far no known deleterious substances have been found in these cements except moisture and air (which epoxies are well known to absorb copiously prior to polymerization).

However, it has now been discovered that these epoxy cements do not make a good permanent bond to copper (and possibly to certain other metals). Grids that had been so cemented could be peeled off after the epoxy had been fully cured, stripping clean from the epoxy cement. The effect has been observed directly in our laboratory and confirmed by one of the major vendors of epoxy resins.

It now seems that this effect, rather than trace impurities in the cement, is the probable reason for the observed degradation of the cells with the epoxy cemented grids. This is borne out by the fact that one of those cells which was originally 3.9% efficient and removed from NASA's

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test after nearly complete degradation and returned to us, was tested and found to be 3.4% efficient. This behavior is characteristic of an intermittent type of contact and indicates that the degradation observed was not in the barrier of the cell but in the package.

It has been found that if the copper grids are electroplated with a thin layer of silver prior to cementing, an excellent bond is obtained to the grid. Additional cells are being fabricated with silver plated copper grids cemented in place using conductive silver epoxy compositions, and these will be submitted for vacuum thermal cycling.

Lamination Process

Recently uncovered evidence has indicated that many of the problems associated with obtaining higher output as well as a more stable cell are located in the lamination area of the process. Photomicrographs of cross-sections of various film cells have frequently shown Capran plastic between the cell barrier and the collector grid. At first this was thought to be primarily a problem of controlling the thickness of the Capran layer, vis-a-vis the thickness of the collector grid, so that there would be just enough Capran to flow between the openings in the grid but not enough to "float" the grid away from the cell.

However, when thickness control was effectively established, evidences of Capran beneath the grid continued. Careful cell dissections were then carried out under the microscope, and it was found that nearly all cells had more than half of the grid contact blocked by an intervening layer of Capran. It appears that the Capran wets and runs under the grid by capillary action while in the molten state of the lamination cycle. The effect of this action is to reduce the collection efficiency of the grid and increase the series resistance of the cell thus reducing efficiency, short circuit current, and fill factor.

In an attempt to alleviate this condition, experiments were run where the lamination temperature was reduced. The idea was that lower temperatures would increase the viscosity of the Capran in its molten state and thus reduce the capillary action of running under the grid. A series of small

area (1 x 2 cm) cells were run at various temperatures. A dramatic increase in cell output was obtained as the lamination temperature was reduced. However, if the temperature was reduced too much, incomplete lamination occurred which first was evidenced first by poor optical coupling between cell and plastic (and reduced cell output), and then by the package opening up.

It appears that only a few degrees separates the region of under lamination from over lamination. In an attempt to make the operation less critical in this respect, longer laminations were tried. This did help, but too long a time can also hurt.

This experiment was then repeated on large area, 50 cm^2, cells of the standard construction. The results are summarized in Table V, and they corroborate the conclusions drawn from the experiments with the small area cells. There is a clear decrease in series resistance which results in an increase in cell efficiency and fill factor. The short circuit current density also improved with decreasing lamination temperature.

Best results were obtained with a lamination temperature of 224°C, as indicated by the control thermocouple embedded in the lamination die, and a hold time of 15 minutes at that temperature. Cell D51E gave an initial efficiency of 7.8% with a short circuit current of 1.2 amperes and a fill factor of 70%. This is the highest output obtained from a CdS solar cell to date. The I-V characteristic curve for this cell is reproduced in Fig. 4. One day later the output of this cell had dropped to 7.3%, as shown.

It appears that the present Clevite process for making large area thin film CdS solar cells is capable of producing cells of 7% air mass 1 sunlight efficiency, but that an improved method of contacting the barrier and packaging the cell is really required.

Alternate Adhesives

The conductive epoxy cemented grid might provide the answer for an improved method of contacting the barrier of the cell. There are several possibilities for an improved method of packaging the cell. One of these possibilities would be to coat the cell, after grid attachment with a

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TABLE V

EFFECT OF LAMINATION TEMPERATURE ON CELL OUTPUT

Lamination Temp. °C	& Time min	Cell No.	OCV v	J (mA/cm^2)	ohms	Fill (%)	Eff. (%)
235	4	D41E	0.48	18.8	0.10	57	5.4
		D41F	0.47	18.8	0.11	54	4.8
		D50A	0.48	20.6	0.10	55	5.5
		D50E	0.46	20.9	0.10	52.5	5.3
		Avg.	0.47	19.8	0.103	55	5.25
228	15	D46D	0.47	19.7	0.09	58	5.9
		D46F	0.47	19.3	0.08	64	5.8
		Avg.	0.47	19.4	0.085	61	5.85
224	15	D51B	0.47	22.4	0.05	70	7.2
		D51D	0.47	23.1	0.05	68	7.4
		D51E	0.47	24.0	0.05	70	7.8
		D51H	0.47	21.5	0.05	68.5	7.0
		Avg.	0.47	22.8	0.050	69	7.35
224	20	D38C	0.47	20.2	0.06	67	6.5
		D38H	0.48	22.0	0.05	68	7.2
		D39C	0.47	20.5	0.07	67	6.4
		D39H	0.47	20.5	0.07	65	6.2
		Avg.	0.47	20.3	0.063	67	6.58

Notes:
All cells 50 cm^2 area, 0.002" thick molybdenum substrates, 20μ thick CdS, encapsulated in 0.002" thick "Mylar" using 0.0005" thick "Capran" adhesive, and 60 lpi copper mesh grids.

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CELL No. *D51E*

AREA = 50.05 cm²

VOLTS

FIG. 4   I-V CHARACTERISTIC CURVE OF
LARGE AREA 7. 8% CELL

% EFF.

MILLIAMPS
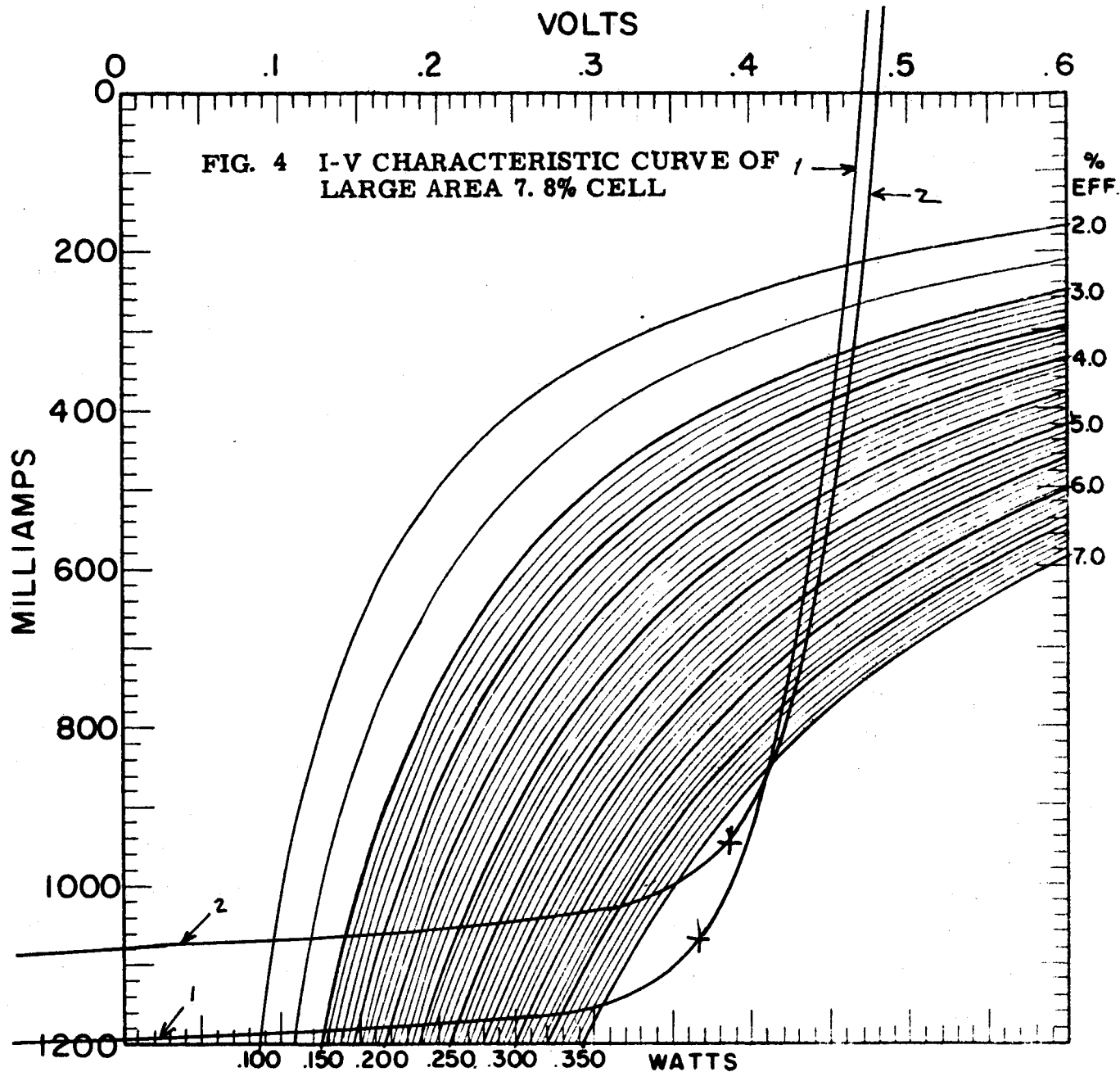
WATTS

TEST NO.	DATE	TIME	OCV	SCC	SERIES Ω	SHUNT Ω	SCC cm²	MAX WATTS	% FILL	% EFF	REMARKS
1	7/22/65	1610	.470	1200			24.0	.391	70	7.8	
2	7/23/65	0815	.480	1080			21.6	.366	71	7.3	
3											
4											
5											
6											
7											
8											
9											
10											
EVAP.	7/20/65	–	STD.								
BARR.	7/21/65	–	STD.								
LAM.	7/22/65	1400	½ C . 2 M - Cu			224° - 15 MIN.					

glossy coating that would act as a moisture barrier and which would stop low energy protons. A separate study to investigate sputtered or evaporated SiO and SiO_2 coatings has been funded by NASA at another laboratory.[10]

Meanwhile, in this laboratory, alternate adhesives to replace Capran are being studied. This work has just gotten underway. Among the adhesives under consideration are polyethylene and Teflon, but other plastic materials will also be checked. The major requirement of this adhesive is that it be hydrophobic, adhere to the cell and to the cover plastic over the range of temperatures which the cell must withstand, that it not be affected by any radiation penetrating the cover plastic, and that it transmit light of the active wavelengths through to the cell.

CELL TESTING

Efficiency Testing

A number of changes have been introduced in the method and tooling for making CdS film cell efficiency measurements. These changes have improved the accuracy, reproducibility and convenience of making these measurements. Additional tooling changes are still in process, hence a more complete and detailed description of this test will be given in the final report on this contract after most of these changes are completed.

In this period an improved cell holding fixture was designed and built. This is a heavy brass block with automatic temperature control, and a vacuum hold-down feature to hold the cell flat, perpendicular to the light and in close physical contact for better heat transfer. Separate non-interacting voltage and current leads are provided and the current lead contact to the cell is made over a large area held under pressure by a toggle action clamp. Temperature is held to 25°C ± 0.5°C by means of thermoelectric cooling and resistance heating elements built into the block.

Light intensity control is maintained by an Eppley modified Mark II radiometer which is monitored by a digital voltmeter just prior to each test. Calibration of the tungsten light intensity to give results equivalent to air mass 1 sunlight has been accomplished by testing a large number of cells in direct sunlight of 80 mW/cm^2 intensity or greater, extrapolating to

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100 mW/cm^2 for each cell, then reproducing the I-V curve for each cell in tungsten light by adjusting its intensity and reading the absolute light intensity on a radiometer. The average radiometer reading for a large number of cells has been taken for calibration of subsequent tests. Separate calibrations have been carried out for Mylar encapsulated and for Kapton encapsulated cells. It has been found that the Kapton encapsulated cells yield an average of 20% less output than the Mylar encapsulated cells.

This method of light calibration may be subject to slight errors, particularly for cells with widely differing spectral responses. However, the present system of measuring CdS film cell output is far more satisfactory than methods previously used, and the Lewis Research Center of NASA has consistently verified the output efficiencies measured by this method.

Hysteresis Effect

Another improvement in cell testing has been the determination of the causes of the so-called hysteresis effect and its elimination from our test results. The hysteresis effect is illustrated in Fig. 5. It is found that when the I-V curve is traced a second time on some cells it does not follow the same path but gives a higher output. The effect generally seems more prominent for poorer cells, but extensive data have not been gathered on this point.

This hysteresis effect is apparently merely a time effect, probably associated with the filling of deep traps, and occurs when the cell has not been illuminated long enough to reach equilibrium.

This is illustrated more clearly by the curve in Fig. 6. Here the same cell of Fig. 5 has been loaded with a 0.6 ohm load (represented by the dashed line of Fig. 5) and the voltage across the load measured as a function of the time after the light was switched on. It is seen that it took about 1-1/2 minutes for the cell output to reach 99% of its final value.

As a result, the test for measuring the I-V curve of our cells has been changed with a time delay relay in the X-Y recorder so that the cell is illuminated for approximately 2 minutes before the curve is traced.

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FIG. 5 HYSTERESIS EFFECT OF I-V CURVE TRACING

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SOLAR BATTERY SECTION
CLEVITE CORP.

CELL No. D27A
AREA = 50.05 cm²

VOLTS

MILLIAMPS

% EFF.
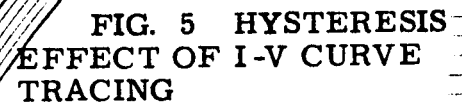
WATTS

TEST NO.	DATE	TIME	OCV	SCC	SERIES Ω	SHUNT Ω	SCC cm²	MAX WATTS	% FILL	% EFF	REMARKS
1	6-23-65	1320									
2											
3											
4											
5											
6											
7											
8											
9											
10											
EVAP.											
BARR.											
LAM											

FIG. 6   TIME RESPONSE OF LARGE AREA CELL WITH FIXED LOAD

Time in seconds

Volts across .5 Ω load

Response Time

Though CdS photoconductors are notorious for having slow response times and even slower decay times, it has been theorized that the photo-voltaic response should be very fast since the barrier seems to be so abrupt. Measurements of the time response of the output of a 1 x 2 cm frontwall metal substrate CdS film cell were made in this period.

A "Strobolume" zenon flash tube was used as a light source, and a photomultiplier tube as a detector for this test. It was found that the rise time for the CdS cell was as fast as that of the light source-photomultiplier combination, which was on the order of a microsecond. The decay time of the CdS solar cell was however somewhat slower, in the range of several hundred microseconds. The curves are shown in Fig. 7.

Figure 7b is an expansion of the time scale of Fig. 7a. The upper curve in each case is that of the light source-photomultiplier combination while the lower curve is of the CdS cell.

Under short circuit conditions the rise time of the CdS was slightly slower than that of the light source -- on the order of 1-1/2 microseconds, and the decay time was somewhat faster than for the open circuit condition.

Temperature Performance

The installation of an automatic temperature control on the test block of the output tester makes it a relatively simple matter to measure the performance of thin film solar cells at different temperatures. In Fig. 8 are plotted the I-V characteristic curves of a 50 cm^2 area 5% CdS film cell at 10° intervals from 10°C to 100°C. There was a steady drop in open circuit voltage, short circuit current, efficiency and fill factor as the temperature increased. These are plotted against temperature in Fig. 9.

This cell was a plastic substrate Mylar encapsulated cell. It is seen that the drop in OCV, SCC, and efficiency over this range is almost linear, but there is an indication that the current may start falling more rapidly at higher temperatures.

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(a) TIME SCALE-40 MICROSECONDS PER DIVISION

(b) TIME SCALE- I MICROSECOND PER DIVISION
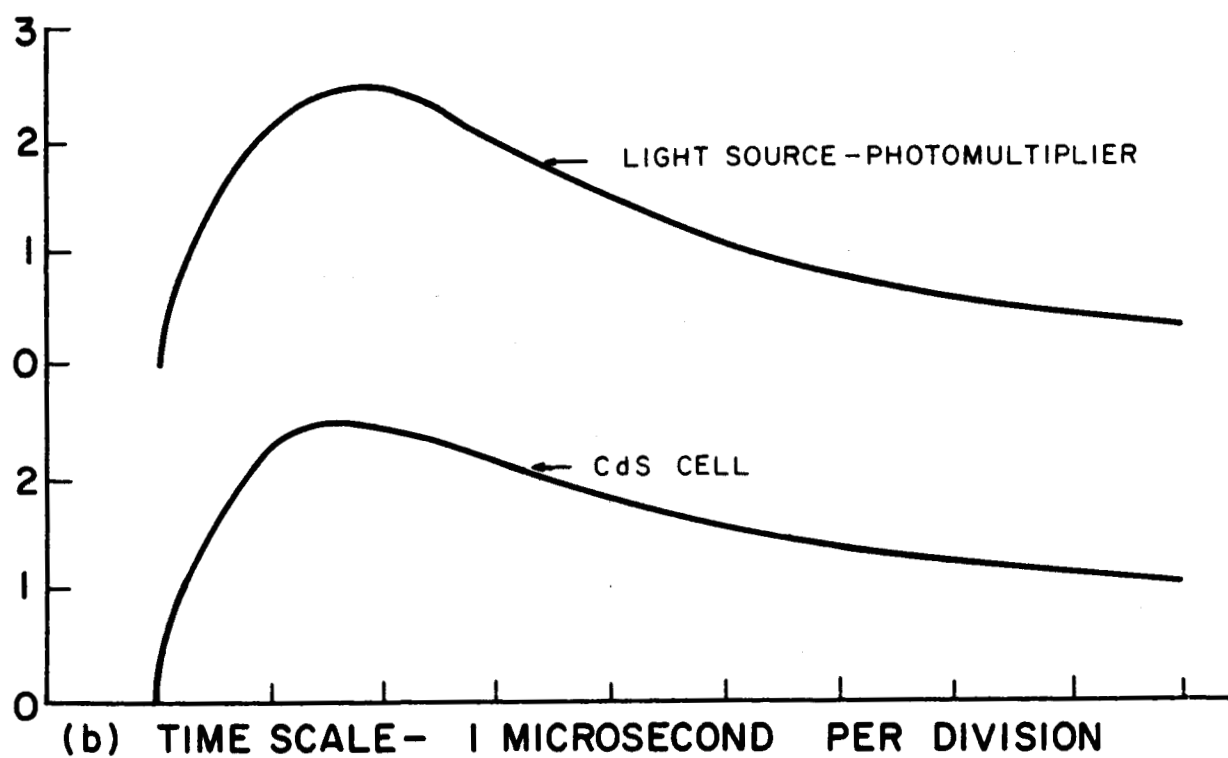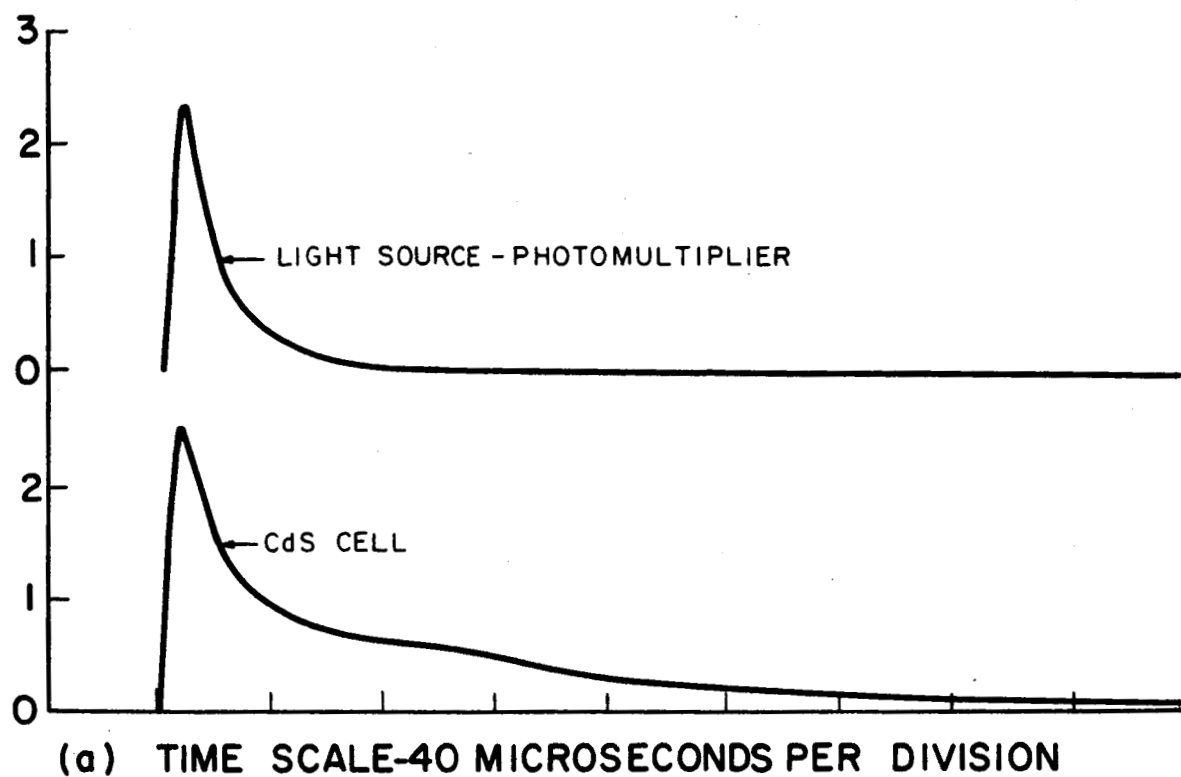
FIG. 7. RISE AND DECAY TIME OF PHOTOVOLTAIC RESPONSE
OF I x 2 cm CdS FILM CELL (OPEN CIRCUIT CONDITION)

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VOLTS

FIG. 8 I-V CURVES OF 5% LARGE
AREA CdS CELL AT VARIOUS
TEMPERATURES FROM 10°C
TO 100°C.

%
EFF.

MILLIAMPS

(Tested in tungsten light
equivalent to 100 mW/cm² sun-
light)

WATTS

SHEET_____ OF ____

TEST NO.	DATE	TIME	OCV	SCC	SERIES Ω	SHUNT Ω	SCC cm²	MAX WATTS	% FILL	% EFF	REMARKS
1	6-25-65	0830	.520	.745			14.9	.275	71	5.5	Temp 10°C
2	"	0844	.508	.725			14.5	.258	70	5.15	Temp 20°C
3	"	0900	.491	.715			14.3	.243	69	4.85	" 30°C
4	"	0930	.475	.700			14.0	.230	69	4.6	" 40°C
5	"	0950	.460	.680			13.6	.215	68.7	4.3	" 50°C
6	"	1016	.448	.670			13.4	.200	66.5	4.0	" 60°C
7	"	1033	.432	.650			13.0	.188	66.9	3.75	" 70°C
8	"	1104	.418	.638			12.75	.170	64.0	3.4	" 80°C
9	"	1125	.405	.620			12.4	.157	63.3	3.15	" 90°C
10	"	1148	.390	.580			11.6	.140	62.0	2.8	" 100°C
EVAP.											
BARR.											

FIG. 9   OCV, SCC, and EFFICIENCY VS. CELL TEMPERATURE
OF 5% PLASTIC SUBSTRATE CELL

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CELL STABILITY STUDIES

Molybdenum Substrate Cells

The major effort planned for the second half of the present contract is to determine and eliminate the major factors causing degradation of CdS film cell output. This is a complex task because there have been widely different degrees of cell degradation experienced, and because there are many conceivable causes for such degradation.

The determination of just how much degradation is normally experienced is in itself difficult because cell design has been changing fairly rapidly in this contract period and because even the tests for measuring cell output have been undergoing evolutionary changes. However, attempts to measure the stability of CdS film cells have been made in this quarter. A few major causes of erratic cell behavior have been uncovered lately, and as a result it is believed that a clearer picture of CdS cell stability is beginning to emerge.

The present "standard" frontwall CdS thin film solar cell is 3" x 3" in size. It is made by vacuum depositing about 20 microns of CdS onto a 40 to 45 micron thick annealed molybdenum foil substrate. A barrier is formed on the CdS surface by dipping the film in a CuCl solution at 90°C for 5 seconds, rinsing in water, and then heat treating for 2 minutes in a 250°C oven. The cell is active at this stage, but its output is difficult to measure accurately. Cells tested at this point in a pressure test rig usually indicate less output than they do after lamination.

Lamination is accomplished by placing a metal grid on the cell barrier, positioning positive and negative leads, sandwiching between two sheets of Mylar plastic using Capran plastic as an adhesive, and fusing with heat and pressure. The Capran flows into the openings of the grid and on cooling holds the grid in intimate pressure contact to the barrier layer. Different metal grids have been evaluated for the purpose. A 60 line per inch, 85% transmissive, electroformed copper mesh approximately 0.0005" thick is in regular use at this laboratory.

While there are wide variations at times, in general we have noted that the photovoltaic power output of these "standard" cells is usually very

low immediately after lamination, but increases steadily over a period of several hours or more until a maximum output is reached. Then there is a slower drop in output characterized by a drop in the short circuit current, and an <u>increase</u> in the open circuit voltage. This latter effect is illustrated in Fig. 10 for a recent cell. This "adjustment" in output is usually nearly complete in a day or so, but in some cases has taken as long as a week. In a few instances the adjustment in SCC and OCV results in a slight increase in output, but more typically a decrease of from 10 to 20% from the peak output is experienced.

The causes of these changes in cell output during the early days of formation are very puzzling. The initial rise in output suggests a second rectifying contact in the cell structure with polarity opposite to the cell barrier. This seems plausible because the first I-V curves frequently show extra inflection points which gradually disappear, and because different metal grids show the effect in characteristically different ways. The explanation for the subsequent "adjustment" is also open. To these authors the pattern suggests a redistribution of impurities or defects in the barrier region causing a change in the density or energy distribution of trapping levels, but supporting data are lacking.

In this laboratory it has been the practice to measure the output of new cells about 2 hours after lamination, or later if indicated, in order to catch the approximate peak of photovoltaic output, and to report this value as the "initial" efficiency. This naturally leads to the highest quotable figures for cell performance. Only recently however has the above described pattern begun to emerge and the validity of this method of cell output characterization come into question.

It would probably be better to wait a few days, or even a week, until the major part of the "adjustment" was complete, and then take the output at that time as the "initial" output of the cell. Up until the present it has been hard to wait a week before measuring the output of cells, because of the rapid pace of the experimental program. It is by no means sure that a week would be sufficient, and even if it was now, this might change radically as cell design and processing continues to evolve. In any case, up to and

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FIG. 10 I-V CURVES OF LARGE AREA FRONTWALL CELL ILLUSTRATING "ADJUSTMENT" OF CURRENT AND VOLTAGE

SHEET _____ OF _____

TEST NO.	DATE	TIME	OCV	SCC	SERIES Ω	SHUNT Ω	SCC cm²	MAX WATTS	% FILL	% EFF	REMARKS
1	7/23/65	1507	.468	1045			20.9	330	67	6.6	
2	7/26/65	0800	.478	955			19.0	310	68	6.2	
3							-				
4											
5											
6											
7											
8											
9											
10											
EVAP.	7/21/65		Std.								
BARR.	7/22/65		Std.								
LAM.	7/23/65	1300	½ mil Capran , 2 mil Mylar , Cu Grid				224°C	15 min			
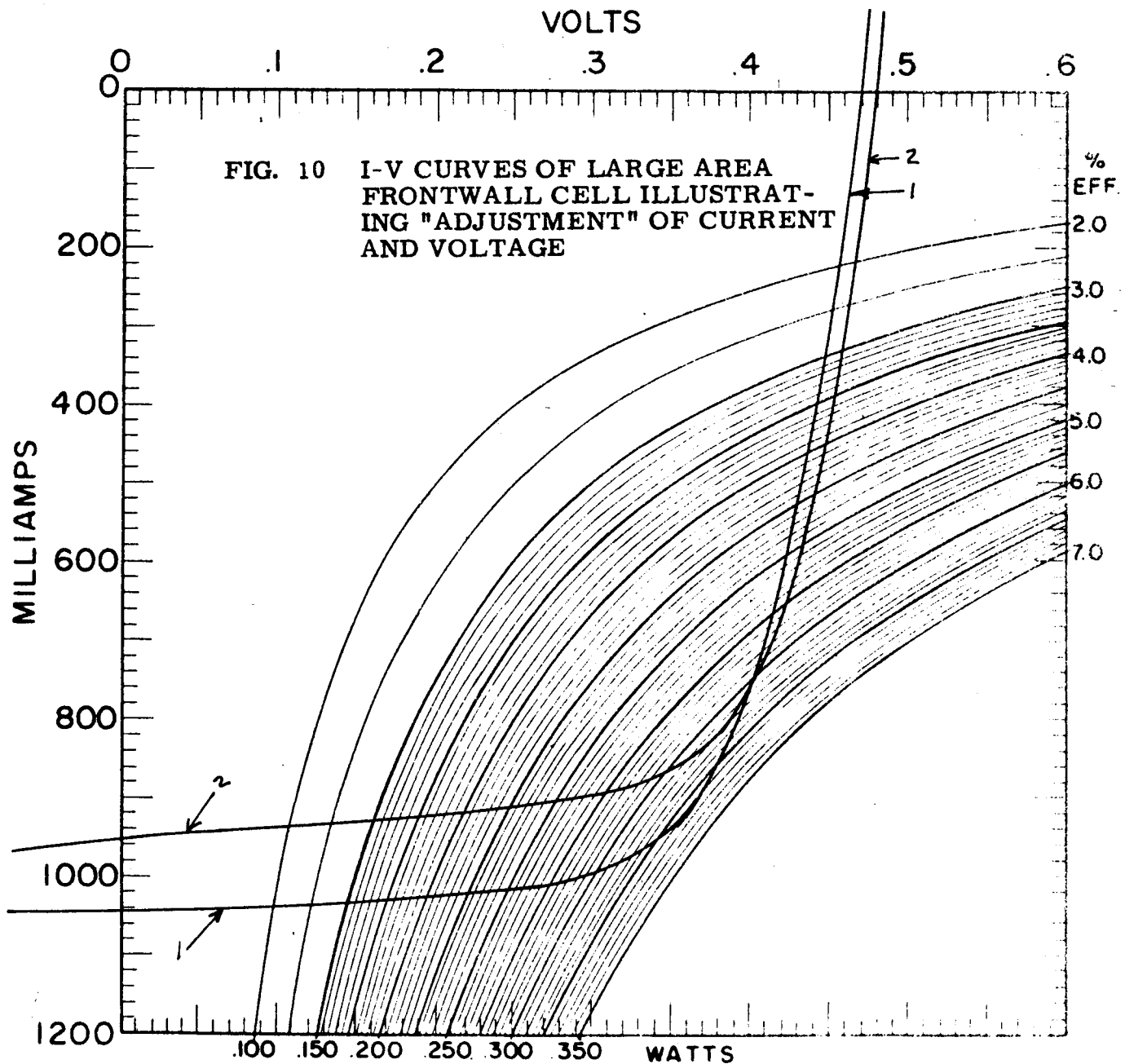
including the present report, the "initial" CdS film cell efficiencies reported have represented the highest output obtained during the first few days of cell life.*

Table VI shows the stability data for standard frontwall molybdenum substrate cells made in the second month of this quarter after the elimination of the output slump which was experienced in the first. Most of these cells showed little or no output change after the first week or so, for periods up to 60 days. A few cells showed extreme degradation, but mostly in the first week of age.

Though proof is lacking, the authors have come increasingly to believe that most of the cases of severe degradation experienced on these cells are attributable to either the absorption of moisture or to the loosening of the grid contact.

The effect of moisture on CdS solar cell barriers has been measured several times by various laboratories and always found to degrade the cells in direct proportion to the amount of moisture involved. It now appears that the Capran used as an adhesive in contact with the cell barrier may greatly aggravate this effect since Capran is hygroscopic. Even when cells are stored in a desiccator it is felt that the Capran competes with the desiccant for the available moisture. If the desiccator is opened periodically, appreciable amounts of moisture may be absorbed by the Capran with consequent cell degradation. This may explain some recent cases of cell degradation experienced with cells stored in cabinet type desiccators, and the apparent immunity to degradation of many cells stored in vacua or placed on continuous load tests.

In the last few weeks we have stored all CdS film cells in "double desiccators". That is, the cells are kept in a closed plastic box containing a desiccant, and the boxes are stored in another desiccator. It is still too early to be definite, but this practice appears to be reducing the amount

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*It is interesting to note that an analogous problem exists in characterizing the voltage output of newly fabricated carbon-zinc dry cells--it being the practice to wait as much as several weeks before attempting to do so.

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of shelf degradation experienced.

Severe moisture degradation can sometimes be verified by attempting to delaminate the cell with a scalpel and tweezers. The adhesive properties of the Capran are greatly damaged by moisture absorption and the layers can then be peeled apart without tearing the grid.

The loosening of the grid contact is discussed in more detail in other sections of this report. Grid loosening of course may also result from moisture pick-up by the Capran and can be particularly deleterious in those cases where some Capran may have run between the grid and the barrier during lamination.

Plastic Substrate Cells

The stability of frontwall Kapton plastic substrate cells, encapsulated with a cover layer of Mylar plastic, appears to be comparable to or slightly better than that of the molybdenum substrate cell. The output stability data of some 14 cells for periods of 18 to 89 days are shown in Table VII.

It is to be noted that the last reading of many of these cells is slightly higher than the previous reading 33 days earlier. This may be due in part to the effect of the extended desiccated storage, but more is probably due to the changes in the method of measuring cell output which were introduced in the interim and which were discussed earlier.

Barrier Fabrication Process

Studies of the effect of the barrier fabrication process on cell stability were started, but definite information on the effect of factors in this area on cell stability have not as yet been obtained. It now seems likely that these factors normally cause second order effects that are largely masked by the first order effects of such things as moisture pick-up and grid loosening. Four separate stages of the barrier fabrication process have been defined for separate investigations into their possible influence on cell instability.

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TABLE VII

STABILITY OF STANDARD FRONTWALL PLASTIC SUBSTRATE CELLS

Days After Lamination

Cell No.	0	15	30	45	60	75	90
A490	5.3	3.6	3.5-3.6	3.8	3.4 3.6		4.3
A491	4.0	3.1	3.3-3.5	3.5	3.5		3.8
A497	5.0-4.9-4.8	5.0	4.8	5.1	4.8	5.5	
A500	5.7	4.9	5.0-5.4-5.3	5.5	5.0	5.7	
A513	4.6	4.4	4.7-4.6	4.8-4.5	4.5	5.2	
A530	4.7-4.7	4.3	4.5-4.0*				
A531	5.2-5.0-4.7	4.8	5.0		5.3		
A538	5.8	5.1	5.4		5.6		
A550	5.4	5.5	5.6		6.1		
A552	5.0	4.6	4.4		4.9		
A554	5.2	4.7	4.5		5.3		
A565	4.7	4.6		5.0			
A568	5.4	4.5		4.8			
D43E	4.8	5.4					

*Delivered to NASA

a. Pre-Treatment of the CdS Surface

Work in this area is meant to include: the effects of strain, dislocations and impurity content in the CdS at the surface of the film; the effect of etching; and the effects of various types of pre-dips. This work has not as yet been started.

b. Barrier Layer Formation

Variations in the barrier formation process were tried to evaluate their effect on cell output and stability. The time of the dip was varied. Earlier indications that times of 5 to 6 seconds gave optimum outputs were verified. Shorter or longer dip times did not improve cell stability.

In another experiment various amounts of $CuCl_2$ were added to the CuCl dip solution, since some of the most stable cells processed nearly a year ago were made when poorer controls over the purity of the CuCl were in effect. Also, digenite, the low temperature form of copper deficient Cu_2S, has a portion of its ions bonded as Cu^{++}. One 3" x 3" film was cut into quarters and each quarter was dipped in barrier solutions containing different amounts of $CuCl_2$ and then finished into cells and tested periodically. The results of this experiment are presented in Table VIII.

Unfortunately, this experiment was run in the early days of the slump in output of standard cells, before it was realized that the slump existed. Hence, the output of the control cell, as well as of the experimental cells, was lower than normal. Even so, there are indications that small amounts of $CuCl_2$ might yield higher initial cell outputs, but there appears to be no real effect on cell stability.

c. Rinsing

The rinse after barrier formation has been studied because it is at this step that residual impurity contaminants are dealt with. The rinse may under some conditions remove beneficial species necessary for cell stability, as well as harmful contaminants.

Normally a short, about 30 seconds, cold distilled water rinse is used after barrier formation, followed by an acetone dip and drying in an argon stream. An experiment was run to study the effect of the time of this

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TABLE VIII

EFFECT OF Cu^{++} ION CONCENTRATION IN BARRIER DIP SOLUTION

	Ratio of Cu^{++} to Cu^{+} ions in Dip Solution			
Days Age	0 (Std)	1/32	1/16	1/8
0	4.2%	4.6%	4.7%	3.7%
1	4.2%	4.6%	4.7%	3.7%
20	3.5%	4.3%	3.9%	3.0%
32	3.7%	4.3%	4.0%	3.4%
112	4.3%	5.1%	4.7%	3.9%

Notes:

12 cm^2 frontwall molybdenum substrate cells cut from film B412B.

Efficiencies measured in 100 mW/cm^2 sunlight equivalent.

Final reading taken with revised measuring set up after three months storage in a double desiccator.

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rinse on output and stability. Again, a 3" x 3" CdS film was cut into quarters, each quarter was rinsed for a different time after barrier formation, the quarters were laminated and checked periodically for output. The data are given in Table IX. Though a single experiment may be misleading, it does indeed appear that too short a rinse is detrimental to both initial output and to cell stability. There is also an indication that too long a rinsing may yield slightly higher cell outputs but at the expense of cell stability. This experiment will be repeated.

Another cell rinsed in a cold water transistor washer for 30 minutes, with the water effluent reaching 18 megohm-cm resistivity, had practically no output.

Hot water rinses appear to be even more severe in their effect than cold water rinses. A 3" x 3" CdS film was cut into quarters and processed with one as a control and three being rinsed in the hot water transistor washer with a temperature of 85°C in the final chamber. The control cell when laminated gave a 6.5% efficiency cell, but each of the hot water rinsed cells gave less than 1% efficiency.

In another test, a 1 x 2 cm film was given a 10 second rinse in hot pure water. When made into a cell it gave less than 1% output.

Several barriers were rinsed in various non-aqueous solvents including acetone, methanol, and ether. All of these rinses destroyed the photovoltaic activity of the cells. This action must be investigated further because an acetone dip is normally used to remove traces of lacquer that is employed to mask portions of cells during the barrier dipping process.

d. Heat Treatment

After barrier formation, the cells are usually given a two minute heat treatment in a 250°C oven. The real function of this step is not known. It is possible that it may finish some chemical reaction at the surface of the cell begun during the dip, that it may be carrying out a fast diffusion of copper from the Cu_2S into the CdS lattice at dislocation sites, or that it may be driving traces of moisture off of the cell. Of course, several of the above may be effected simultaneously.

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TABLE IX

EFFECT OF POST BARRIER RINSE TIME

		Rinse Time		
Days Age	10 Sec.	30 Sec. (Std)	1. 5 Min.	4. 5 Min.
0	4. 3%	6. 5%	6. 5%	6. 7%
1	2. 7%	6. 0%	6. 4%	5. 9%
2	< 1. 0%	5. 2%	5. 6%	4. 8%
18	< 1. 0%	4. 5%	5. 4%	4. 6%
175	< 1. 0%	4. 5%	--	4. 4%

Notes:

12 cm^2 frontwall molybdenum substrate cells cut from film B352D.

Efficiencies measured in 100 mW/cm^2 sunlight equivalent.

Final reading taken with revised measuring set-up after five months storage in a double desiccator, (Cell B352D-3 not available for final reading).

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A careful study of the effect of shorter and longer heat treatments and of heat treatments at lower and at higher temperatures would be desirable. However, such a study would be difficult at present because the wide variations from other aspects of the cell fabrication process would probably mask the effects expected from the study. Therefore this study is being put off for a more propitious time.

One experiment was run that might be expected to show measurable effects. This was the storage of several cells in vacuum at 100°C for an extended period in an attempt to see if diffusion effects were occurring. Two standard molybdenum substrate cells (from the slump period) and two plastic substrate cells, all 3" x 3" in size, were selected. One of the plastic cells had a nickel plating and the other a zinc plating on the conductive coating of the substrate. They were aged 3 days or more in a desiccator prior to the test.

The cells were kept in a vacuum of about 10^{-3} Torr and were removed and tested after periods of 1 hour, 2 hours, 1 day, 4 days and 11 days. All four of the cells degraded appreciably (25 to 35%). However, it is not clear why this occurred. The degradation of the molybdenum substrate cells occurred mostly after the first day of storage while the plastic substrate cells showed appreciable degradation in the first hour. The data are given in Table X. More data are needed here to determine if this effect is due to mechanical failure of the package or to a change in the photovoltaic barrier.

Other aspects of the post barrier heating and aging that have been looked into in an exploratory way without any indication of major effects are: storage of the cells in the dark between the barrier application and cell lamination steps; no post heat treatment after barrier application; various times of storage between barrier application and cell lamination; and carrying out the heat treatment in nitrogen rather than in air.

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TABLE X

EFFECT OF HIGH TEMPERATURE VACUUM STORAGE

Time	Molybdenum Substrate Cells		Plastic Substrate Cells	
	Cell A502	Cell B439A	Cell A506 (Ni)	Cell A507 (Zn)
0	3.65%	3.30%	4.65%	4.65%
1 hour	3.70	3.60	4.15	4.20
2 hours	3.75	3.50	4.00	4.15
1 day	3.55	3.55	4.05	4.30
4 days	3.30	3.20	3.90	4.00
11 days	2.40	2.50	3.35	3.60

PLASTIC SUBSTRATE CELL

Cell Design

During the quarter a number of changes were made in the design of the frontwall plastic substrate cell to give a lighter weight construction, larger area utilization, reduced curling and improved appearance.

The previous nickel plating of the conductive silver-Pyre M. L. coating of the substrate has been eliminated (since nickel is unacceptable for space) and replaced by a zinc plating from a fluoborate bath.

The negative lead is now an integral extension of the conductively coated substrate. It is 3" wide and extends 3/8" beyond the active portion of the cell. The positive lead is an 0.001" thick gold plated silver foil tab attached to the collector grid and extending 3/8" beyond the edge of the cell. The positive and negative leads are on opposite edges and this arrangement facilitates testing of the cells and will also facilitate their interconnection into arrays.

The electroformed gold mesh collector grid has been replaced by an electroformed copper mesh grid. While copper does not give any more output to the cell, it is more economical and is easier to handle.

The lower encapsulating plastic layer has been eliminated and the plastic substrate itself now acts as the lower half of the encapsulating package. This makes a lighter weight thinner package with less tendency to curl. The thickness of the CdS film has also been reduced to about 20 microns. The zinc plated silver-Pyre M. L. substrate appears to present a finer grained more uniform textured surface for the evaporated CdS film which apparently makes the thinner CdS film practical. There have been indications that CdS film thicknesses as low as 10 to 15 microns may be practical with this construction, but there has not been time to investigate this adequately. The thinner CdS films seem to have eliminated the previous tendency for the CdS layers to form stress cracks.

Processing

There were no major changes in the processing of the plastic sub-strate cells in this period. The attention in processing was directed

primarily to improved tooling and to the factors causing non-uniformity. Larger quantities of cells were fabricated and these steps have been very beneficial in improving yields as well as cell output.

During the last month or so revised design substrate holders permitted the plastic substrate films to be evaporated in the NRC evaporator where up to nine such 3" x 3" films can be handled at a time. Previously these were done in the Veeco on a one-at-a-time basis. A direct comparison of cell efficiencies from films evaporated in the two different evaporators disclosed no differences. Hence, standard fabrication runs are now all being handled in the NRC equipment, usually 2 or 4 at a time (with the balance being molybdenum substrate films), while the Veeco equipment is being reserved for special experiments into the evaporation process.

Performance of Standard Large Area Cells

Table XI lists the large area plastic substrate cells fabricated according to the steadily evolving standard design and process during the third quarter of the contract. In the first month 7 cells were fabricated and these averaged 5. 0% with a minimum of 4. 0% and a maximum of 5. 7%.

In the second month 15 cells were fabricated and these averaged 5. 4% with a minimum of 4.7% and a maximum of 7. 1%. In this month average cell active area increased from 44 cm^2 to 48 cm^2.

In the third month there were a lot more cells fabricated, 32 cells, and these were done on a more routine basis with less individual attention and special handling. As a result there were more lower output cells (flawed films not being rejected in process, etc.) and the average output was off somewhat to 4. 9%. There was one shorted cell, but the remaining cells ranged between 3. 2% and 6. 2%. The average active cell area was increased to 49. 8 cm^2.

For the entire third quarter, average cell efficiency was 5. 1% (versus 3. 0% for the second quarter), active area was 47 cm^2 (vs. 41 cm^2), short circuit current density was 16. 0 mA/cm^2 (vs. 11. 6), and the fill factor was 64. 4% (vs. 57%).

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TABLE XI

OUTPUT OF LARGE AREA FRONTWALL PLASTIC SUBSTRATE CELLS -- Third Quarter

A - First Month

Cell No.	Active Area cm^2	OCV v	J (mA/cm^2)	Fill %	Eff. %
A490	43. 5	. 50	17. 0	62	5. 3
A491	46. 0	. 49	12. 6	65	4. 0
A497	41. 0	. 49	15. 6	65	5. 0
A500	41. 3	. 47	18. 9	64	5. 7
A506	44. 6	. 48	15. 9	66	5. 1
A507	45. 3	. 47	15. 8	69	5. 1
A513	46. 7	. 48	16. 7	58	4. 6
Avg.	44	.48	15.9	64	5.0

B - Second Month

Cell No.	Active Area cm^2	OCV v	J (mA/cm^2)	Fill %	Eff. %
A530	47. 5	. 49	16. 1	63	5. 0
A531	50. 5	. 49	16. 5	64	5. 2
A534	49. 0	. 49	16. 7	67	5. 4
A538	49. 2	. 50	17. 3	67	5. 8
A540	45. 9	. 48	17. 3	69	5. 7
A552	48. 6	. 47	15. 8	67	5. 0
A548	46. 1	. 48	17. 2	69	5. 7
A550	44. 7	. 49	17. 5	71	5. 9
A553	49. 4	. 48	16. 4	68	5. 4
A554	49. 0	. 49	15. 5	69	5. 2
A563	48. 4	. 47	16. 9	62	4. 9
A565	47. 6	. 45	17. 2	61	4. 7
A566	50. 0	. 49	16. 6	62	5. 0
A568	49. 3	. 51	17. 0	62	5. 4
A570	49. 1	. 49	21. 7	67	7. 1
Avg.	48.3	.48	16.6	66	5.4

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TABLE XI (Cont'd)

C - Third Month

Cell No.	Active Area cm^2	OCV v	J (mA/cm^2)	Fill %	Eff. %
A536	45.0	.50	15.5	69	5.3
A574	51.1	.47	18.7	66	5.9
A575	49.3	.49	17.4	68	5.8
A579	49.9	.47	17.1	66	5.3
A582	51.0	.47	14.0	55	3.7
A583	49.6	.50	14.4	68	4.9
A587	48.8	.48	15.1	58	4.2
A588	49.8	.49	13.4	65	4.2
A589	48.3	.48	14.2	68	4.6
A590	50.2	.50	15.0	60	4.5
A592	50.0	.50	15.4	58	4.5
A593	50.8	.48	15.6	69	5.0
A598	49.3	.48	13.3	58	3.7
A600	50.6	.49	15.1	62	5.0
A601	49.6	.50	14.1	63	4.4
A605	49.1	.48	16.0	62	4.7
A609	49.8	.49	13.1	50	3.2
A610	50.7	.50	14.8	63	4.6
A611	49.0	.49	14.7	69	4.9
B456I	49.5	.44	17.6	61	4.7
D31I	49.8	.50	14.1	69	4.8
D33D	50.3	.47	18.1	63	5.4
D35I	50.7	.47	15.8	67	4.9
B463I	50.0	.50	17.8	66	5.9
D37I	50.3	.49	20.4	59	6.0
D38I	49.6	.49	14.7	53	3.8
D41I	50.2	.49	15.7	61	4.8
D42I	51.8	.52	15.9	56	4.6
D43E	50.3	.50	15.4	66	5.2
D45C	50.0	.49	18.7	68	6.2
D45I	50.0	.48	18.4	67	5.9
D46C	shorted				
D47C	50.0	.49	18.2	70	6.2
Avg.	49.8	.49	15.4	63.2	4.9
Avg. for Qtr.	47.4	.48	16.0	64.4	5.1

So far the major emphasis has been to improve the output and reproducibility of the plastic substrate cell so that it would be on a par performance-wise with the molybdenum substrate cell. This objective has just about been achieved and it now appears that there is little essential difference in the output obtainable from the two constructions. Now more attention can be given to comparing the relative advantages inherent in the different constructions. One of the major potential advantages to the plastic substrate cell is lighter weight, since the thickness of the plastic can presumably be reduced to the minimum required for structural integrity and the thickness of the conductive coating can be reduced to the minimum required to carry the current from the cell.

The best calculated power-to-weight ratio for these 3" x 3" CdS thin film solar cells was experienced for one of the plastic substrate cells fabricated this period. Cell No. A570 weighed 2.51 grams and produced initially 0.304 watts at 100 mW/cm^2. This represents 88 watts per pound on the basis of a linear extrapolation of the output to 140 mW/cm^2 light intensity input.

METAL SUBSTRATE CELL

    a.   Process

        The process for fabricating the frontwall molybdenum substrate cell has remained essentially unchanged during this period except for minor tooling changes to enable larger quantities of cells to be fabricated. The various improvement and process studies described elsewhere in this report were run as special experiments and the regular process remained unchanged as a baseline to compare against.

        The only process changes that did occur were in the CdS vacuum evaporation operation, and these have been described earlier. It is expected that the studies of the parameters of the lamination process will lead to process changes in that operation in the following quarter and to a further increase in the average cell output.

b. Performance of Standard Large Area Cells

Two distinct phases of cell performance were encountered during this report period. The first, occuring at the beginning of the quarter and lasting just over a month, was a slump in cell output from the previous 5% average level to approximately 3.5% average. The second was the restroation of standard process line cells to the 5% level.

The reasons for the early low efficiencies are still not completely understood. Just prior to the period the NRC evaporator was re-tooled to give nine 3" x 3" size films per evaporation in place of the previous four films. At the same time minor changes in the barrier formation and the cell lamination steps were introduced to speed up these operations, and some additional personnel were secured and trained in these operations.

At first it appeared that these changes were completely successful and that average cell efficiency was holding steady at the 5% level. However, thereafter cell output dropped, in stages, and remained low and variable for about a month. As a result fewer films and cells were fabricated, the yield was lower, and the experimental program was delayed.

Throughout the period a number of experiments and tests were run in an attempt to determine the cause for the drop in cell efficiency. The situation was complicated by a change to a new lot of CdS raw material, by difficulties with faulty evaporation sources from the vendor, and by possible contamination from the shields and tooling used in the evaporator. Corrective actions were taken in all of these areas as well as in the other processing steps where changes had been made. These corrective actions were taken mostly simultaneously, and hence when cell outputs emerged from the slump, it could not be ascertained which causes had been at fault.

The data on the standard frontwall metal substrate cells fabricated in this period are summarized in Table XII. All cells were standardized at 50 cm^2 area. The plastic encapsulation was 0.002" thick in all cases, of "Mylar" or "Kapton" as shown. It is to be noted that while the average output for the Mylar encapsulated cells remained at the 5% level during the third month, the variability in this month was severe with many

TABLE XII

OUTPUT OF STANDARD LARGE AREA METAL SUBSTRATE
CELLS - Third Quarter

A - Mylar Encapsulated

Period	No. of Cells	< 3%	3.0 to 3.9%	4.0 to 4.9%	5.0 to 5.9%	6.0 to 6.9%	Summary		
							Min.	Max.	Avg.
1st month*	19	4	7	8	0	0	2.6%	4.5%	3.7%
2nd month	25	0	0	9	16	0	4.3	5.9	5.0
3rd month	42	2	2	17	12	9	2.6	6.8	5.0
Total Quarter	86	6	9	34	28	9	2.6	6.8	4.7

*slump period

B - Kapton Encapsulated

Period	No. of Cells	< 2%	2.0 to 2.9%	3.0 to 3.9%	4.0 to 4.9%	5.0 to 5.9%	Summary		
							Min.	Max.	Avg.
1st month	3	0	0	1	2	0	3.2%	4.1%	4.0%
2nd month	7	0	0	4	3	0	3.7	4.3	4.0
3rd month	24	4	4	8	8	0	1.5	4.8	3.4
Total Quarter	34	4	4	13	13	0	1.5	4.8	3.6

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high and low output cells. It is believed that this reflects the variability in the lamination process, and that when this variability is eliminated a new higher level of efficiency will result. The same comments are believed to apply to the Kapton encapsulated cells as well.

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